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Study of magneto-electroluminescence and magneto-conductance in polymer light-emitting electrochemical cells

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Magneto-electroluminescence (MEL) and magneto-conductance (MC) have been investigated in polymer light-emitting electrochemical cells based on "super-yellow" poly-(phenylene vynilene) (SY-PPV). We measured positive MEL(B) and MC(B) responses that show a modified Lorentzian shape for $B < 120$ mT. At $B < 2$ mT, both MEL(B) and MC(B) responses show a second component, opposite in sign to the higher field response. We interpret the magnetic field response using the polaron pair model, from which we extract the hyperfine interaction constant of polarons in the SY-PPV polymer. © *2011 American Institute of Physics*. [doi:10.1063/1.3605251]

Recently, magneto-electroluminescence (MEL) and magneto-conductance (MC) responses have been studied in a variety of non-magnetic organic light emitting diodes (OLEDs).[1–10] These novel magnetic field effects (MFE) in OLEDs have attracted ample experimental and theoretical studies that have been mainly focused on revealing the underlying mechanism of the effect. To date, however, the exact mechanism is still debated.[1–13]

Polymer light-emitting electrochemical cells (PLECs) provide an attractive alternative to OLEDs due to their simple structure and use of air-stable electrodes.[14,15] A typical PLEC consists of a luminescent polymer blended with mobile positive and negative ions, sandwiched between two electrodes. Because of the relatively slow turn-on time constant caused by the slow ion diffusion in the active layer and the short lifetime, the application of PLECs for dynamic display is scarce. Recently, Yu *et al.* demonstrated a "chemical stabilized" PLEC through chemical cross-linking of an ion-transport material, which has relatively fast turn-on and long lifetime.[17] This type of PLEC device is promising since is stable and fast enough for display and further research studies. In this work, we investigate MEL and MC responses in chemical stabilized PLECs and discussed their underlying mechanism in comparison with MFE in regular OLED devices.

The PLECs (Fig. 1(a) inset) were prepared on clean indium tin oxide (ITO) patterned glass substrates in a nitrogen glove box. For the active polymer, we used the π-conjugated polymer alkoxyphenyl substituted poly(1,4-phenylene vinylene) and dubbed "super-yellow" poly-(phenylene vynilene) (SY-PPV, Merker) because of its strong photoluminescence band ~550 to 650 nm (Fig. 1(b) inset). The ion transport materials were trimethylolpropane trimethacrylate (TMPTMA, Sigma-Aldrich) and salt lithium trifluoromethane sulfonate ($LiCF_3SO_3$, Sigma-Aldrich) (Fig. 1(a) inset). SY-PPV, TMPTMA, and $LiCF_3SO_3$ (20:10:1) were dissolved in anhydrous, inhibitor-free tetrahydrofuran (THF) at room temperature, with a polymer concentration of ~5.5 mg/ml. The solution mixture was subsequently spin-coated directly onto an ITO substrate, and the device was capped with an evaporated Al electrode.

The MEL and MC response measurements were performed in an optical cryostat. The field, **B** was applied parallel to the device electrodes. Both responses were measured at constant applied voltage while sweeping the field B. MC and MEL are defined as $\Delta I/I = (I(B)\text{-}I(B = 0))/I(B = 0)$ and $\Delta EL/EL = (EL(B)\text{-}EL(B = 0))/EL(B = 0)$, respectively.

The PLEC device was initially biased at $V = 15$ V for about 30 min "activation" period, where the ITO was positively biased. Figure 1(a) shows the current and light emission intensity at room temperature, as a function of the biasing time, t up to ~30 min; after which the device performance stabilized. During this time period, the current and EL intensity increase gradually with t, showing long-time transient characteristics typical of PLEC devices.[16] Upon cell activation, the mobile positive and negative ions redistribute to form thin electric double layers close to the opposite electrode interfaces (Fig. 1(a) inset). Subsequently, the active interlayer is electrochemically doped; p-type next to the ITO anode and n-type near the Al cathode. The two doped layers thickness increase with the activation time and, finally, a stable light-emitting p-i-n junction is formed close to the device center (Fig. 1(a) inset). At the same time, the TMPTMA molecules are polymerized into a rigid, covalently cross-linked network that loses its ionic mobility while forming a chemical stabilized PLEC.[17] At this stage, the injected holes and electrons reach the polymer interlayer at the center, where polaron pairs (PPs) are formed on the polymer chains in both triplet $(PP)_T$ and singlet $(PP)_S$ spin configurations. The $(PP)_S$ specie is a precursor to intrachain singlet excitons that emits light, whereas $(PP)_T$ forms intrachain triplet exciton that undergoes non-radiative recombination.

Figure 1(b) shows the current-voltage and EL brightness-voltage dependencies of a PLEC device at room temperature, following the activation period. At this stage, the device shows an excellent rectification ratio, unipolar current and EL emission characteristics, which indicates formation of a stabilized p-i-n junction following charge separation during the device initiation period.[18]

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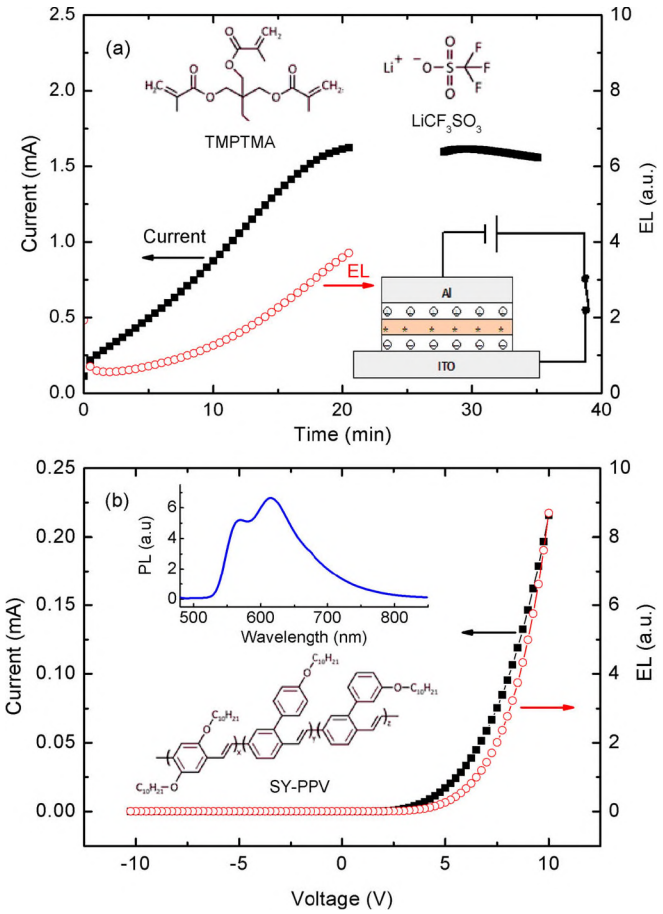

FIG. 1. (Color online) (a) The current (solid squares) and light emission intensity (open circles) as a function of the charging time during the cell activation process. The upper inset shows the chemical structures of TMPTMA and $LiCF_3SO_3$; the lower inset shows the device structures, and the p-i-n junction formed following the cell activation. (b) The current-brightness-voltage curves of PLEC devices at room temperature, after the cell activation. The inset shows the photoluminescence spectrum of the SY-PPV polymer of which chemical structure is given.

Figure 2 shows the MEL(B) and MC(B) responses of the PLEC device measured at several bias voltages at room temperature. Above the turn-on bias voltage of ~3 V, the device shows positive MEL and MC. Both responses increase nonlinearly with B, where the half-field at half-maximum (HFHM) $B_{1/2}$ increases approximately linearly with V (Fig. 3(b)). At B~120 mT (close to saturation) and $V = 4$ V, we measured MEL and MC of ~5.6% and ~0.4%, respectively; these values may be favorably compared with those obtained in more conventional OLEDs.

Both MEL(B) and MC(B) responses can be reasonably fit using the modified Lorentzian expression[2] $f(B,B_0) \sim B^2/(|B| + B_0)^2$ (Figs. 2(a) and 2(b)), where B_0 was found to increase approximately linearly with V (Fig. 3(b)); this is in parallel with $B_{1/2}(V)$ discussed above. At low V, we obtained B_0 of ~4-5 mT, which is in good agreement with B_0 values obtained in MEL response of OLED devices.[2] Both shape and fitting expression of the MEL and MC responses in PLEC are similar to those in OLEDs, where it was shown that models based on the HFI spin-Hamiltonian explain well the B dependencies.[3,6,9–11,13] We thus conclude that the MFEs in PLECs have similar origin as those in OLEDs.

We have also investigated the MEL(B) and MC(B) responses in PLECs at low field, $B < 3$ mT (Fig. 2(a) and 2(b) insets). As clearly seen, both responses reverse sign at $B < 1$ mT, forming a pronounced minimum at B_{min}(MEL) ≈ 0.7 mT and B_{min}(MC) ≈ 0.8 mT. This low-field component was also observed in OLED devices, and both low and high field components were recently shown to originate from the same PP spin-Hamiltonian that contains both hyperfine and Zeeman interactions, where the most strongly coupled nuclei spin are explicitly taken into account.[10,13] We also obtained the ratio $r = B_{min}/B_{1/2}$ of 0.07 for EL and 0.09 for MC, in good agreement with r~0.08 in OLEDs.[10]

In the traditional view of the MC in OLEDs, the injected spin $^1/_2$ carriers form weakly bound PPs on the polymer chains. The PP spin Hamiltonian contains the two polaron spins, most strongly coupled nuclear spins, the HFI, and Zeeman contribution term. As B increases, the intermixing between the PP/nuclei spin sublevels substantially changes due to the increased Zeeman contribution to the Hamiltonian, thereby affecting their respective populations.[13] This leads to a monotonous $MC_M(B)$ response, which also depends on the PP recombination rate, k.[11,13] In a simpler PP model that describes pairs of radical ions, it was empirically realized that $B_{1/2}$ scales with the HFI constant, a. In fact a semi-empirical law was advanced, which for opposite charge radicals with same a reads[19]

$$B_{1/2} \approx 2a[I(I+1)]^{1/2}, \quad (1)$$

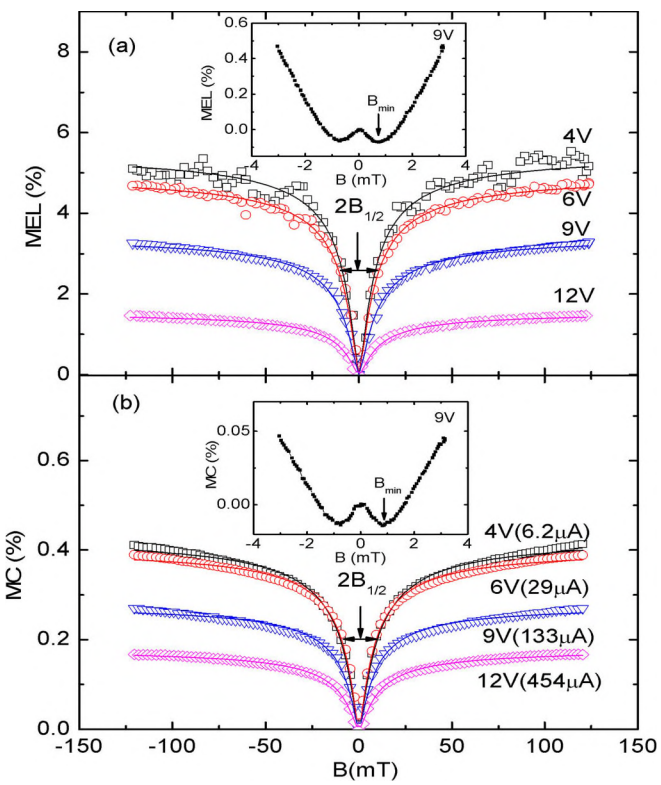

FIG. 2. (Color online) (a) MEL(B) and (b) MC(B) room temperature responses of the PLEC at various bias voltages, V up to $B = 120$ mT. The lines through the data points are fits using a modified Lorentzian model (see text). $B_{1/2}$ is the HFHM of the response, as indicated. The insets show the low-field response of MEL and MC up to $B = 3$ mT, where $B_{min} \approx 0.75$ mT.

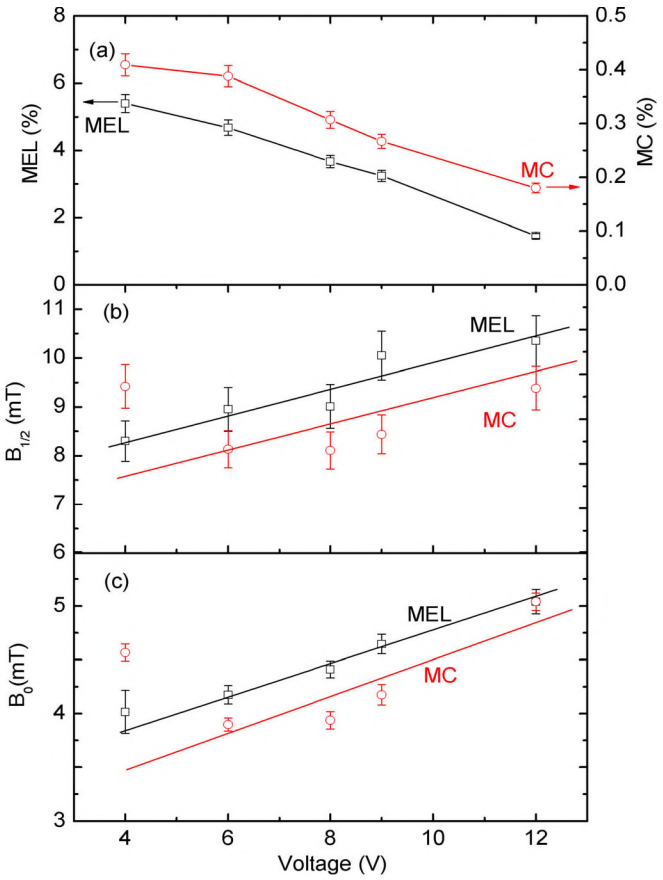

FIG. 3. (Color online) (a) The voltage dependencies of MEL and MC at $B = 120$ mT. (b) and (c) The voltage dependencies of the parameters $B_{1/2}$ and B_0 for the MEL and MC responses, extracted from Figs. 2(a) and 2(b), respectively. The lines through the data points are linear fits to guide the eye.

where I is the nuclear spin quantum number. We may use Eq. (1) to extract the HFI constant a from the MEL(B) and MC(B) responses. We obtained (Fig. 3(a)) an average $B_{1/2} \approx 9.5$ mT for both responses at 9 V, and from Eq. (1) with $I = 1/2$, we find $a \approx 5.5$ mT. This HFI constant is larger than that found in poly(2,5-dioctyloxy-p-phenylenevinylene) (DOO-PPV) polymer ($a \sim 3.5$ mT (Ref. 14)) presumably because the side group in SY-PPV contains a benzene ring very close to the intrachain carbon atoms, where the polaron wavefunction is substantial and this increases the HFI.

If the exchange interaction constant, J between the bound polarons in the PP specie is finite, then a new $MC_{LC}(B)$ component emerges at $B \approx B_{LC} = J$, where a singlet-triplet level-crossing (LC) occurs, giving rise to excess spin intermixing between the PP spin sublevels.[15] The $MC_{LC}(B)$ component has, therefore, an opposite sign with respect to the regular $MC_M(B)$ response, which results in a strong MC(B) modulation response at $B = B_{LC}$.[10] This essentially describes the low-field MC(B) response obtained in PLEC, except that the LC does not occur due to the exchange interaction within the PP species, but it is caused by a LC between the spin-sublevels of the interaction Hamiltonian at B = 0 (Ref. 10) and causes the MC(B) and MEL(B) responses to change sign at $B_{min} > 0$. We, thus, conjecture that the full magnetic field response in PLEC can be in fact explained by the more sophisticated PP model used successfully in OLEDs.[10,13]

Two important findings are noteworthy regarding the MFE in PLECs. (i) First, the MC value is about one order of magnitude smaller than the MEL (Fig. 2). This is different from the responses in OLEDs in which the MEL and MC are of comparable magnitude. According to the PP model, the MC mostly results from the formation and dissociation of oppositely charged PPs. In an imbalanced organic diode such as the present PLEC, the PP formation probability depends on the minority carriers, whereas the current depends on the majority carriers. In this case, only few injected majority carriers form PPs; many majority carriers pass through the organic interlayer without PP formation. These carriers contribute to the overall current density but do not contribute to the MC.[12] In contrast, EL comes from $(PP)_S$, and therefore, MEL is directly proportional to the PPs that are formed in the device regardless whether or not the device is current balanced. We, therefore, conjecture that the low MC value in PLEC is caused by the imbalanced device characteristics. (ii) Second, both MEL(B) and MC(B) responses weaken and broaden with V. Figure 3(a) summarizes the voltage dependence of MEL and MC in PLECs. The MEL and MC fall from 5.6% and 0.41%, respectively, at $V = 4$ V, to 1.5% and 0.18%, respectively, at $V = 12$ Volt. Also $B_{1/2}$ of both MEL and MC responses increase approximately linearly with V (Fig. 3(b)). This effect was also observed in OLEDs.[13] A consistent explanation for this effect has not been given yet, but we speculate that the high electric field in the device may change the PP effective recombination rate, k and this, in turn may broaden the MFE response.[13]

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